



Taatjes, C. A., Khan, M. A. H., Eskola, A. J., Percival, C. J., Osborn, D. L., Wallington, T. J., & Shallcross, D. E. (2019). Reaction of Perfluorooctanoic Acid with Criegee Intermediates and Implications for the Atmospheric Fate of Perfluorocarboxylic Acids. *Environmental Science and Technology*, 53(3), 1245-1251.  
<https://doi.org/10.1021/acs.est.8b05073>

Peer reviewed version

Link to published version (if available):  
[10.1021/acs.est.8b05073](https://doi.org/10.1021/acs.est.8b05073)

[Link to publication record in Explore Bristol Research](#)  
PDF-document

This is the author accepted manuscript (AAM). The final published version (version of record) is available online via ACS at <https://pubs.acs.org/doi/10.1021/acs.est.8b05073> . Please refer to any applicable terms of use of the publisher.

## University of Bristol - Explore Bristol Research

### General rights

This document is made available in accordance with publisher policies. Please cite only the published version using the reference above. Full terms of use are available:  
<http://www.bristol.ac.uk/red/research-policy/pure/user-guides/ebr-terms/>

## Reaction of Perfluorooctanoic Acid with Criegee Intermediates and Implications for the Atmospheric Fate of Perfluorocarboxylic Acids

Craig A. Taatjes,<sup>1,\*</sup> M. Anwar H. Khan,<sup>2</sup> Arkke J. Eskola,<sup>1,3</sup> Carl J. Percival,<sup>4,5</sup> David L. Osborn,<sup>1</sup> Timothy J. Wallington,<sup>6</sup> Dudley E. Shallcross<sup>2,7,\*</sup>

<sup>1</sup>Combustion Research Facility, Mail Stop 9055, Sandia National Laboratories, Livermore, California 94551-0969 USA; <sup>2</sup> School of Chemistry, The University of Bristol, Cantock's Close BS8 1TS, UK; <sup>3</sup>Molecular Science, Department of Chemistry, University of Helsinki, FI-00560 Helsinki, Finland; <sup>4</sup>The Centre for Atmospheric Science, The School of Earth, Atmospheric and Environmental Science, The University of Manchester, Simon Building, Brunswick Street, Manchester, M13 9PL, UK; <sup>5</sup>Jet Propulsion Laboratory, California Institute of Technology, 4800 Oak Grove Drive, Pasadena, CA 91109 USA; <sup>6</sup> Research & Advanced Engineering, Ford Motor Company, Dearborn, MI 48121 USA. <sup>7</sup>Department of Chemistry, University of the Western Cape, Robert Sobukwe Road, Bellville 7535, South Africa.

*Abstract:* The reaction of perfluorooctanoic acid with the smallest carbonyl oxide Criegee intermediate, CH<sub>2</sub>OO, has been measured and is very rapid, with a rate coefficient of  $(4.9 \pm 0.8) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ , similar to that for reactions of Criegee intermediates with other organic acids. Evidence is shown for the formation of hydroperoxymethyl perfluorooctanoate as a product. With such a large rate coefficient, reaction with Criegee intermediates can be a substantial contributor to atmospheric removal of perfluorocarboxylic acids. However, the atmospheric fates of the ester product largely regenerate the initial acid reactant. Wet deposition regenerates the perfluorocarboxylic acid via condensed-phase hydrolysis. Gas-phase reaction with OH is expected principally to result in formation of the acid anhydride, which also hydrolyzes to regenerate the acid, although a minor channel could lead to destruction of the perfluorinated backbone.

\*Authors to whom correspondence should be addressed: [cataatj@sandia.gov](mailto:cataatj@sandia.gov) (CAT), [D.E.Shallcross@bristol.ac.uk](mailto:D.E.Shallcross@bristol.ac.uk) (DES).

Perfluorocarboxylic acids (PFCAs) are a class of compounds with the general formula  $C_xF_{2x+1}COOH$  that are ubiquitous in the environment.<sup>1</sup> The smallest member of the series, trifluoroacetic acid (TFA), has both natural and man-made sources.<sup>2</sup> The larger members of the series have no known natural sources and are present in the environment solely as a result of human activities. It has been shown previously that reaction with Criegee Intermediates is an important gas-phase atmospheric fate of trifluoroacetic acid<sup>2</sup> and other organic acids.<sup>3-5</sup> We extend this work by reporting a study of the longer-chain member of the series perfluorooctanoic acid (PFOA;  $C_7F_{15}COOH$ ).

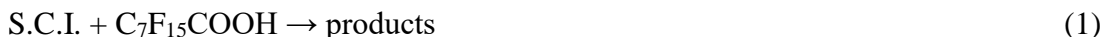
PFOA was used for more than 60 years to provide surface coatings for industrial and consumer products, as a surfactant in fluoropolymer production, and in fire-fighting foams. It is a highly persistent chemical<sup>6</sup> and bioaccumulates in birds,<sup>7</sup> fish,<sup>8</sup> and humans.<sup>9</sup> The Persistent Organic Pollutants Review Committee of UNEP at its thirteenth meeting<sup>10</sup> recommended to the Conference of the Parties to list PFOA and its salts and PFOA-related compounds in Annex A or B of the Stockholm Convention. The production and use of PFOA was phased-out by the chemical industry in 2015.<sup>11</sup>

In addition to direct industrial emissions, PFCAs arise from the degradation of fluorotelomer alcohols with the generic formula  $F(CF_2)_nCH_2CH_2OH$ , where  $n$  is an even number.<sup>6, 12, 13</sup> These alcohols are used in oil and water repelling coatings and waxes<sup>13</sup> and have a lifetime of around 20 days, allowing significant hemispheric transportation.<sup>12</sup> Indeed, PFOA and other PFCAs have been observed in terrestrial<sup>14</sup> and aquatic remote environments.<sup>15, 16</sup> Indoor air may contain higher PFOA concentration than that in outdoor air because there is estimated to be 10-20 times higher concentrations of fluorotelomer alcohols in the indoor environment.<sup>17-19</sup>

In the atmosphere it is believed that reaction of PFOA with oxidants such as the OH radical is too slow to be an important loss process. The reaction of PFOA with OH occurs at ambient temperature with a rate coefficient of  $1.7 \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ ,<sup>20</sup> so the lifetime with respect to OH loss would be *ca.* 68 days.<sup>21</sup> Direct photolysis in the troposphere is small because the UV absorption of PFOA is at short wavelength,<sup>22</sup> so wet and dry deposition were believed to be the main removal processes of PFOA. Based on an effective Henry's law coefficient of  $2.46 \times 10^3 \text{ mol L}^{-1} \text{ atm}^{-1}$  and a global average dry deposition velocity of  $1.9 \text{ mm s}^{-1}$ , the lifetime of PFOA with respect to wet deposition and dry deposition has been estimated to be 17 and 48 days, respectively,<sup>6</sup> giving an overall lifetime of around 12 days. Recently it has been reported that carbonyl oxide Criegee intermediates ( $CH_2OO$ ,  $CH_3CHOO$  and  $(CH_3)_2COO$ ) react at or even above the gas-kinetic limit with organic and inorganic acids.<sup>2-4, 23</sup>

Criegee intermediates (C.I.) are reactive zwitterionic species that are formed during the ozonolysis of alkenes in solution<sup>24, 25</sup> and in the gas phase. In the last few years the gas-phase reactivity of thermalized "stabilized Criegee intermediates" (S.C.I.) with a variety of potential atmospheric co-reactants (e.g.  $SO_2$ ,  $H_2O$  and  $NO_2$ ) has been determined directly by different research groups, which has been reviewed in several recent papers.<sup>26-30</sup> Preliminary estimates

suggest that levels of some Criegee intermediates can be as high as  $1 \times 10^5 \text{ cm}^{-3}$  in indoor<sup>31</sup> and outdoor environments<sup>27, 30, 32</sup> and therefore, if reaction (1) has a rate coefficient similar to those determined for other organic acids<sup>2-4</sup> then it could be a significant or even dominant loss process.



In this study the direct determination of the rate coefficient for the reaction of perfluorooctanoic acid with the simplest S.C.I.,  $\text{CH}_2\text{OO}$ , has been made at room temperature and around 4 Torr total pressure. We use the STOCHEM-CRI<sup>33-35</sup> atmospheric chemistry and transport model to investigate reaction (1) as a chemical loss process of PFOA and quantify its significance compared with the other physical and chemical loss processes of PFOA. Reaction (1) is assumed to be an insertion of the S.C.I. into the O-H bond of PFOA as suggested for other carboxylic acids;<sup>3</sup> the atmospheric implications of the product are also discussed.

## Experiment

The  $\text{CH}_2\text{OO}$  reaction with PFOA was investigated using the Sandia multiplexed photoionization mass spectrometry apparatus at the Advanced Light Source of Lawrence Berkeley National Laboratory. Additional measurements for the rate constant determination were carried out at Sandia National Laboratories using a hydrogen discharge lamp (10.2 eV) for photoionization. The  $\text{CH}_2\text{OO}$  Criegee intermediate is formed from the reaction of  $\text{O}_2$  with  $\bullet\text{CH}_2\text{I}$  radical, produced by pulsed 351 nm laser photolysis of diiodomethane<sup>36</sup>, and detected by synchrotron photoionization and time-of-flight mass spectrometry (TOF-MS), following the experimental methods of Welz and coworkers.<sup>4, 36, 37</sup> The decay of the resulting  $\text{CH}_2\text{OO}$  Criegee intermediate is measured as a function of PFOA concentration. The PFOA is delivered in a flow of He that passes through a thermostatically controlled ( $T = 20^\circ\text{C} / 293.15 \text{ K}$ ) mixing vessel, a “U-tube” filled with solid PFOA powder ( $\geq 95\%$ ) mixed with sand (quartz sand, 50-70 mesh particle size). The concentration of PFOA in the flow is calculated from the pressure in the mixing vessel and the experimentally determined vapor pressure curves of PFOA.<sup>38, 39</sup> From the literature we estimate uncertainty in PFOA vapor pressure of  $\sim 5\%$ . The mixing vessel was held below the temperature in the laboratory where experiments were performed to prevent PFOA condensation downstream. Also, measurements at various PFOA concentrations were performed in a random order and no sign of any “memory effect” was observed, suggesting PFOA adsorption on the delivery system was unimportant under the experimental conditions.

Uncertainties in the individual pseudo-first order rate coefficient determinations are empirically judged to be  $\pm 15\%$  based on repeated measurements at the same concentration of PFOA. The initial concentration of  $\text{CH}_2\text{OO}$  is estimated as  $\sim 1\text{-}2 \times 10^{11} \text{ cm}^{-3}$ ; because of the very fast kinetics of  $\text{CH}_2\text{OO} + \text{PFOA}$  reaction and limitations on the time response of the experimental system, the measurements at the lowest PFOA concentrations do not meet usual criteria for the pseudo-first order limit. The uncertainty at the lowest concentrations is taken to be

correspondingly larger (up to  $\pm 30\%$ ), and that uncertainty is reflected in the overall final rate coefficient determination.

## Modeling

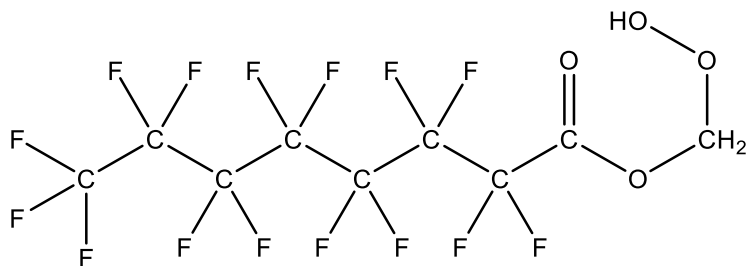
The Global Chemistry Transport Model, CRI-STOCHEM used in this study has been described in detail elsewhere.<sup>33-35, 40, 41</sup> The S.C.I. concentration was estimated by considering its production through the ozonolysis reactions of the modeled alkenes (ethene, propene, *trans*-but-2-ene, isoprene,  $\alpha$ -pinene,  $\beta$ -pinene) and loss through unimolecular reaction, and the reactions with water and water dimer. The rate constants for the reactions between alkenes and  $O_3$  were taken from the Master Chemical Mechanism (MCM) (<http://mcm.leeds.ac.uk/MCM>). The rate constants for the loss of S.C.I. with water and water dimer were taken from the literature.<sup>42</sup> Steady state concentrations of S.C.I. ranging from zero to  $6.0 \times 10^5$ , with average of  $1.5 \times 10^4$   $\text{cm}^{-3}$ , are estimated in our model study.<sup>5, 27</sup> The global distribution of the lifetime of PFOA with respect to the loss by reaction with S.C.I. and the global reduction in lifetime factor of PFOA ((loss by OH + deposition loss)/(loss by OH + deposition loss + loss by S.C.I.)) was estimated under the assumption that reactions of all Criegee intermediates with PFOA occur with the same rate coefficient as that determined for  $k_1$  (at least for reactions of organic acids the rate coefficients with stabilized C1 and C2 Criegee intermediates are known to be similar).<sup>4</sup>

## Results and Discussion

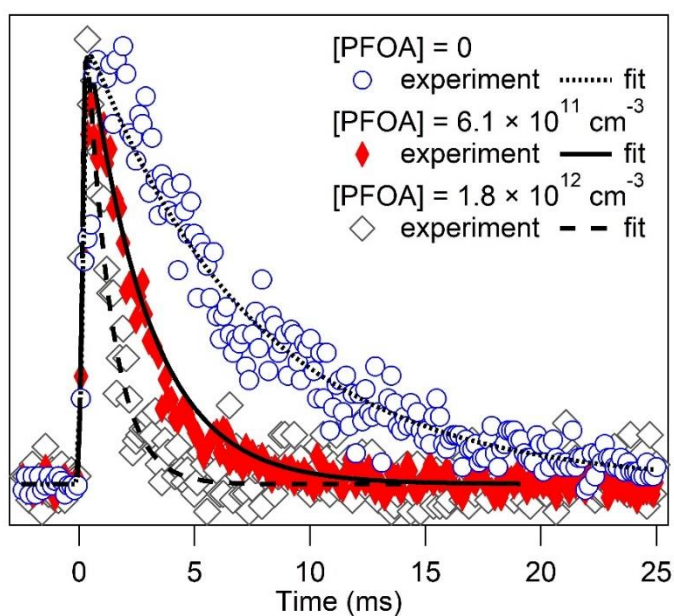
### Kinetics

Figure 1 shows traces of  $\text{CH}_2\text{OO}$  signals at various PFOA concentrations. An exponential decay is employed to fit the data, and the decay constants are plotted against the PFOA concentration in Figure 2. The linear fit to this plot, weighted by the estimated uncertainties in the individual determinations (with larger uncertainty for the lowest-concentration measurements as described above), returns the second-order rate coefficient for the reaction of  $\text{CH}_2\text{OO}$  with PFOA,  $k_1 = (4.9 \pm 0.8) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$  (95% uncertainty bounds). The reactivity of  $\text{CH}_2\text{OO}$  towards PFOA is similar to that with TFA,<sup>2</sup>  $k = (3.4 \pm 0.3) \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ , and consistent with the general behavior of carbonyl oxides towards organic acids, which shows a strong dependence on the dipole moment of the acid. A structure-activity relationship (SAR) based on a dipole-dipole capture model<sup>3</sup> predicts a rate coefficient of  $2.9 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$ , about 60% lower than the present experimental measurement, a reasonable level of agreement for the SAR prediction.

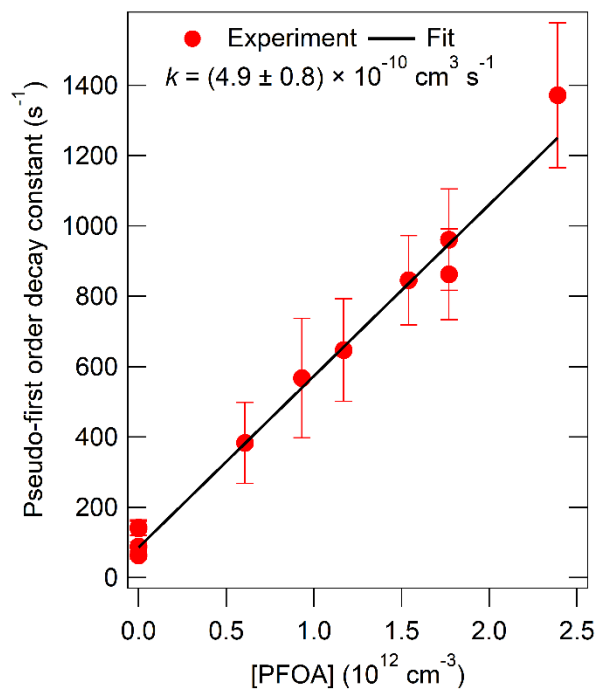
The reactions of carbonyl oxides with organic acids are calculated<sup>43, 44</sup> and observed<sup>3</sup> to proceed by insertion to form hydroperoxyesters. Theory shows that this 1,4-insertion is barrierless, resulting in large rate coefficients, as observed experimentally.<sup>43</sup> By analogy, the reaction of  $\text{CH}_2\text{OO}$  with PFOA should form a hydroperoxymethyl perfluorooctanoate (Scheme I), which we abbreviate to HPMPFO.



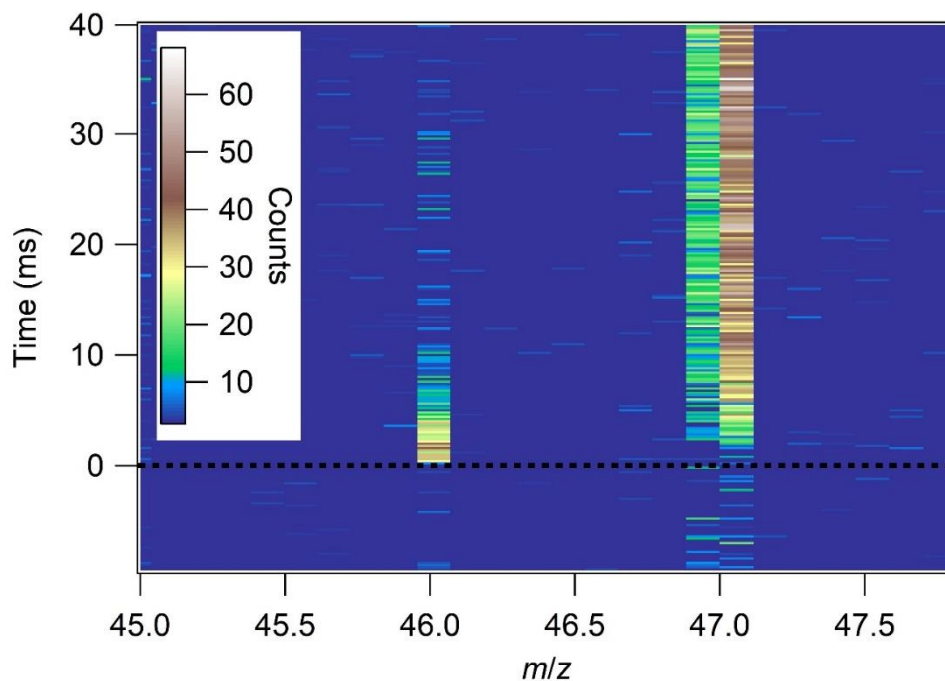
Scheme I: hydroperoxymethyl 2,2,3,3,4,4,5,5,6,6,7,7,8,8,8-pentadecafluorooctanoate (HPMPFO)



**Figure 1.** Measured decay of photolytically produced  $\text{CH}_2\text{OO}$ , detected by 10.2 eV photoionization, for several concentrations of PFOA. Fits to an exponential decay function are shown as the lines.



**Figure 2.** Plot of the pseudo-first order decay constants, acquired from fits as shown in Figure 1, versus the concentration of PFOA. The slope of the fitted line gives the second-order rate coefficient for CH<sub>2</sub>OO removal by PFOA.

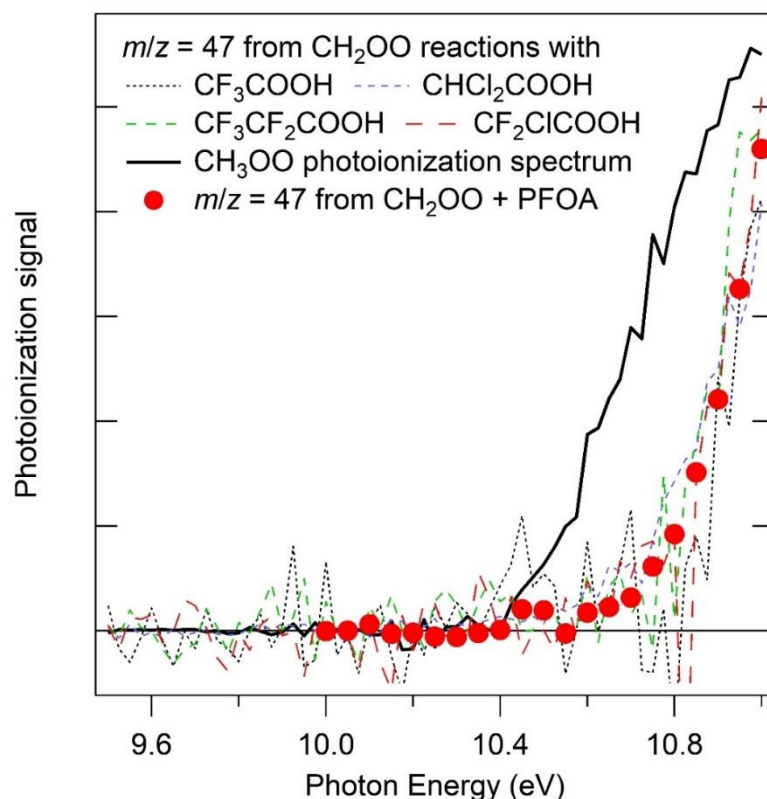


**Figure 3.** Time behavior of signals for the CH<sub>2</sub>OO reactant ( $m/z = 46$ ) and a fragment ion of the product ( $m/z = 47$ ) of reaction 1.

The HPMPFO product has a mass of 460 amu. A search for product signal around the flight time corresponding to a cation at  $m/z = 460$  was not successful (see Figures S1 and S2); but the fragment protonated carbonyl oxide is observed at  $m/z = 47$ , with a rise time corresponding to the decay time of  $\text{CH}_2\text{OO}$  (Figure 3). The kinetic profile matches that of a stable product; the hydroperoxymethyl esters formed in reactions of Criegee intermediates with other acids have been observed to dissociatively ionize to yield a protonated Criegee intermediate.<sup>3</sup>

Photoionization signals at the parent mass for other hydroperoxymethyl esters are often small or unobservable,<sup>3, 4, 45</sup> although the hydroperoxymethyl-2,2,2-trifluoroacetate from  $\text{CH}_2\text{OO}$  reaction with trifluoroacetic acid does show a parent ion signal.<sup>3</sup> Figure 4 compares the photoionization spectrum of this fragment ion to  $m/z = 47$  fragment ions from hydroperoxymethyl esters formed in several other Criegee intermediate reactions. The similarity in the spectra suggests substantial commonality in the dissociative ionization process of these analogous molecules. The neutral  $\bullet\text{CH}_2\text{OOH}$  radical is essentially unbound<sup>46, 47</sup> and direct ionization of this species cannot be the source of the stable product spectrum. Moreover, the spectrum is not consistent with direct ionization of the more stable  $\text{CH}_3\text{OO}\bullet$  radical.<sup>48</sup>

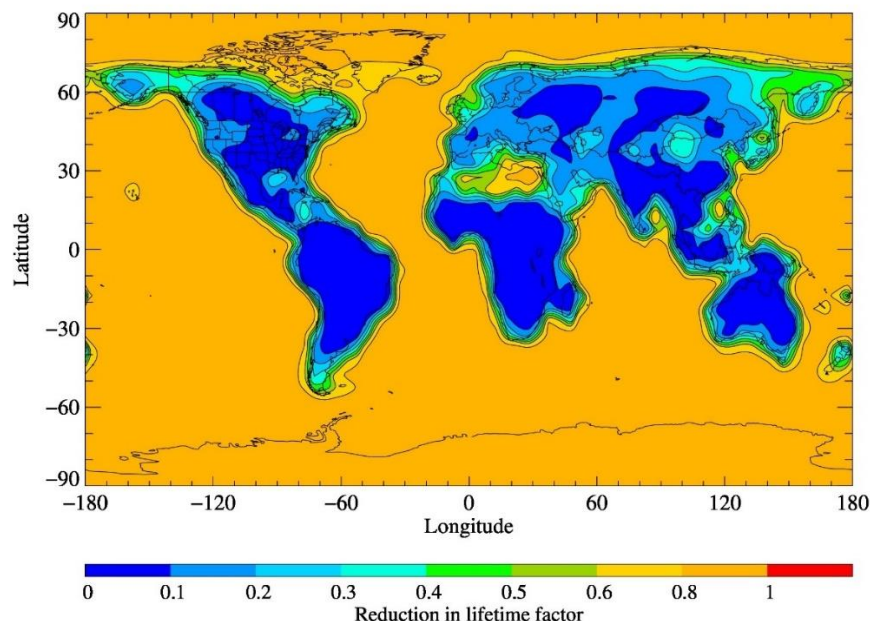




**Figure 4.** Photoionization spectrum for the  $m/z = 47$  fragment ion from the HPMPFO product of reaction 1, compared to spectra for similar products from  $\text{CH}_2\text{OO}$  reactions with other halogenated acids <sup>3</sup> and the direct photoionization spectrum of the methylperoxy radical <sup>48</sup>.

### Modeling

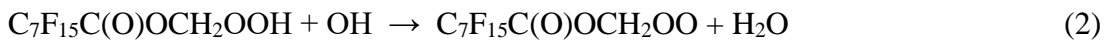
Combining the value of  $k_1$  measured here and a global annual average S.C.I. concentration of  $1.5 \times 10^4 \text{ cm}^{-3}$  gives a lifetime of PFOA with respect to loss by reaction with S.C.I. of 1.7 days. Given that the global model is likely to underestimate the level of Criegee intermediates, especially in regions of high ozone and high alkene (urban outflow and where high biogenic emissions meet elevated ozone),<sup>49</sup> the impact of reaction (1) as a loss process compared with other loss processes (e.g. loss by OH, wet deposition and dry deposition) could be substantial, reducing its lifetime by more than 90% in high S.C.I. regions (Figure 5). Over much of the Earth the reaction with Criegee intermediates are likely to be the dominant loss process for PFOA and similar perfluorinated carboxylic acids.



**Figure 5.** The reduction in lifetime factor due to the reaction of S.C.I. with PFOA. Reduction in lifetime factor is the ratio of the literature sum of loss processes (loss by OH + deposition loss) to the revised sum of loss processes (loss by OH + deposition loss+ loss by reaction with S.C.I.)

However this rapid loss does not necessarily correspond to permanent removal of PFOA, and assessment of atmospheric consequences demands consideration of the set of possible fates for HPMPFO. The University of Manchester UManSysProp tool,<sup>50</sup> which applies group contribution methods<sup>51, 52</sup> to estimate vapor pressures, predicts the vapor pressure of HPMPFO to be ~ 40 times smaller than that of the PFOA reactant, which may lead to increased nucleation and secondary organic aerosol formation over terrestrial regions.<sup>3</sup> If the product is taken up into atmospheric aqueous phases including cloud, fog and aerosol liquid water, expected to occur on a time scale of approximately 5-15 days,<sup>53</sup> rapid hydrolysis<sup>54</sup> is expected to regenerate PFOA and hydroperoxymethanol or formic acid. The net effect of the reaction would then be largely to accelerate the wet deposition of PFOA and convert the Criegee intermediates into aqueous-phase products. Hydroperoxysters in general are also expected to be lost from the atmosphere by reaction with OH radicals. Hydrogen abstraction from the OO-H bond would be expected to occur with a rate constant of approximately the value of  $(0.5-1.0) \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$  observed for the analogous reaction with methyl hydroperoxide.<sup>55</sup> Combining this rate constant with  $[\text{OH}] = 1 \times 10^6 \text{ cm}^{-3}$  gives an estimate of ~1-2 days for the atmospheric lifetime of HPMPFO with respect to reaction with OH. A rate coefficient of  $k(\text{OH}+\text{HPMPFO}) = 4.8 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$  is calculated using the Estimation Programs Interface (EPI) Suite developed by the United States Environmental Protection Agency;<sup>56</sup> for this rate coefficient the estimated lifetime against reaction with OH is about 2½ days.

Reaction of HPMPFO with OH is conceivably important for PFOA destruction because in the presence of NO it could lead to “unzipping” of the fluorinated alkyl chain by the following mechanism:<sup>12</sup>



However, unless reaction (4a) is substantially more rapid than reaction (4b), the reaction of PFOA with Criegee intermediates will largely form the acid anhydride  $\text{C}_7\text{F}_{15}\text{C}(\text{O})\text{OCHO}$ , which will hydrolyze to regenerate PFOA



and not initiate atmospheric perfluorocarboxylic acid degradation. Measurements of degradation in the analogous  $\text{CF}_3\text{C}(\text{O})\text{OCH}_3$  system<sup>57</sup> suggest that reaction of the fluoroalkoxy radical with  $\text{O}_2$  (4b) will be far more important than dissociation (4a). Further investigation of the reactions of HPMPFO or similar hydroperoxyfluoroesters is required to completely understand the mechanism of atmospheric removal.

The results presented here for PFOA, combined with previous results for TFA, show that reaction with Criegee intermediates is the dominant gas-phase atmospheric fate of perfluorocarboxylic acids over land masses. The concentration of reactive alkenes and hence Criegee intermediates drops off sharply over the ocean and Criegee intermediate chemistry is less important. The reactions of perfluorocarboxylic acids  $\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{OH}$  with general Criegee intermediates  $(\text{R}_1)(\text{R}_2)\text{COO}$ , where  $\text{R}_1$  and  $\text{R}_2$  denote an H atom or a hydrocarbon radical group, produce hydroperoxyfluoroesters of the general formula  $\text{C}_x\text{F}_{2x+1}\text{C}(\text{O})\text{OC}(\text{R}_1)(\text{R}_2)\text{OOH}$ . These will in turn be removed by uptake into atmospheric aqueous aerosols and reaction with OH radicals. Uptake into aqueous aerosols will be followed by hydrolysis to reform the perfluorocarboxylic acid,<sup>54</sup> with a net effect the same as direct uptake of the perfluorocarboxylic acid into the aqueous aerosol. However, reaction with OH radicals, expected to occur on a time scale of 1-2 days, will likely lead to regeneration of the gas-phase perfluorocarboxylic acid, with at most a minor contribution from oxidative degradation into  $\text{CO}_2$  and HF. As a consequence, reactions with S.C.I. are unlikely to be a substantial overall loss mechanism for gas-phase atmospheric perfluorocarboxylic acids. Further modeling studies are needed to quantify the global impact of such reactions as an atmospheric fate for perfluorocarboxylic acids.

## Acknowledgements

The laboratory chemical kinetics studies and the participation of CAT, AJE, and DLO was supported by the Division of Chemical Sciences, Geosciences and Biosciences, Office of Basic Energy Sciences (BES), U.S. Department of Energy (USDOE). We thank Rebecca Caravan for scientific advice during preparation of this manuscript and Kendrew Au for technical support of the experimental measurements. Atmospheric modeling was supported by NERC (grant codes-NE/K004905/1, NE/I014381/1 and NE/P013104/1) and Bristol ChemLabS (MAHK, DES). Part of this research was carried out by the Jet Propulsion Laboratory, California Institute of Technology, under contract with the National Aeronautics and Space Administration (NASA). CJP was supported by the NASA Upper Atmosphere Research and Tropospheric Chemistry programs. The Advanced Light Source is supported by the Director, Office of Science, BES/USDOE under Contract No. DE-AC02-05CH11231 at Lawrence Berkeley National Laboratory. Sandia National Laboratories is a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the USDOE's National Nuclear Security Administration under contract DE-NA0003525. This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the USDOE or the United States Government.

Ford Motor Company (Ford) does not expressly or impliedly warrant, nor assume any responsibility, for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, nor represent that its use would not infringe the rights of third parties. Reference to any commercial product or process does not constitute its endorsement. This article does not provide financial, safety, medical, consumer product, or public policy advice or recommendation. Readers should independently replicate all experiments, calculations, and results. The views and opinions expressed are of the authors and do not necessarily reflect those of Ford. This disclaimer may not be removed, altered, superseded or modified without prior Ford permission.

**Supporting Information.** Figures S1 and S2.

## References

1. Prevedouros, K.; Cousins, I. T.; Buck, R. C.; Korzeniowski, S. H., Sources, Fate and Transport of Perfluorocarboxylates. *Environ. Sci. Technol.* **2006**, *40*, (1), 32-44.
2. Chhantyal-Pun, R.; McGillen, M. R.; Beames, J. M.; Khan, M. A. H.; Percival, C. J.; Shallcross, D. E.; Orr - Ewing, A. J., Temperature - Dependence of the Rates of Reaction of Trifluoroacetic Acid with Criegee Intermediates. *Angew. Chem. Int. Ed.* **2017**, *56*, (31), 9044-9047.
3. Chhantyal-Pun, R.; Rotavera, B.; McGillen, M. R.; Khan, M. A. H.; Eskola, A. J.; Caravan, R. L.; Blacker, L.; Tew, D. P.; Osborn, D. L.; Percival, C. J.; Taatjes, C. A.; Shallcross, D. E.; Orr-Ewing, A. J., Criegee Intermediate Reactions with Carboxylic Acids: A Potential Source of Secondary Organic Aerosol in the Atmosphere. *ACS Earth Space Sci.* **2018**, *2*, (8), 833-842.
4. Welz, O.; Eskola, A. J.; Sheps, L.; Rotavera, B.; Savee, J. D.; Scheer, A. M.; Osborn, D. L.; Lowe, D.; Booth, A. M.; Xiao, P.; Khan, M. A. H.; Percival, C. J.; Shallcross, D. E.; Taatjes, C. A., Rate Coefficients of C1 and C2 Criegee Intermediate Reactions with Formic and Acetic Acid Near the Collision Limit: Direct Kinetics Measurements and Atmospheric Implications. *Angew. Chem. Int. Ed.* **2014**, *53*, (18), 4547-4550.
5. Khan, M. A. H.; Lyons, K.; Chhantyal-Pun, R.; McGillen, M. R.; Caravan, R. L.; Taatjes, C. A.; Orr-Ewing, A. J.; Percival, C. J.; Shallcross, D. E., Investigating the Tropospheric Chemistry of Acetic Acid Using the Global 3-D Chemistry Transport Model, STOCHEM-CRI. *J. Geophys. Res. Atmos.* **2018**, *123*, (11), 6267-6281.
6. Wallington, T. J.; Hurley, M. D.; Xia, J.; Wuebbles, D. J.; Sillman, S.; Ito, A.; Penner, J. E.; Ellis, D. A.; Martin, J.; Mabury, S. A.; Nielsen, O. J.; Sulbaek Andersen, M. P., Formation of C<sub>7</sub>F<sub>15</sub>COOH (PFOA) and Other Perfluorocarboxylic Acids during the Atmospheric Oxidation of 8:2 Fluorotelomer Alcohol. *Environ. Sci. Technol.* **2006**, *40*, (3), 924-930.
7. Kannan, K.; Choi, J.-W.; Iseki, N.; Senthilkumar, K.; Kim, D. H.; Masunaga, S.; Giesy, J. P., Concentrations of perfluorinated acids in livers of birds from Japan and Korea. *Chemosphere* **2002**, *49*, (3), 225-231.
8. Martin, J. W.; Mabury, S. A.; Solomon, K. R.; Muir, D. C. G., Dietary accumulation of perfluorinated acids in juvenile rainbow trout (*Oncorhynchus mykiss*). *Environ. Toxicol. Chem.* **2003**, *22*, (1), 189-195.
9. Kannan, K.; Corsolini, S.; Falandysz, J.; Fillmann, G.; Kumar, K. S.; Loganathan, B. G.; Mohd, M. A.; Olivero, J.; Wouwe, N. V.; Yang, J. H.; Aldous, K. M., Perfluorooctanesulfonate and Related Fluorochemicals in Human Blood from Several Countries. *Environ. Sci. Technol.* **2004**, *38*, (17), 4489-4495.
10. United Nations Environment Programme *Report of the Persistent Organic Pollutants Review Committee on the work of its thirteenth meeting* UNEP/POPS/POPRC.13/7; United Nations: 2017; p 27.
11. DuPont DuPont position statement on PFOA. <http://www.dupont.com/corporate-functions/our-company/insights/articles/position-statements/articles/pfoa.html> (September 2018),
12. Ellis, D. A.; Martin, J. W.; De Silva, A. O.; Mabury, S. A.; Hurley, M. D.; Sulbaek Andersen, M. P.; Wallington, T. J., Degradation of Fluorotelomer Alcohols: A Likely Atmospheric Source of Perfluorinated Carboxylic Acids. *Environ. Sci. Technol.* **2004**, *38*, (12), 3316-3321.
13. Styler, S. A.; Myers, A. L.; Donaldson, D. J., Heterogeneous Photooxidation of Fluorotelomer Alcohols: A New Source of Aerosol-Phase Perfluorinated Carboxylic Acids. *Environ. Sci. Technol.* **2013**, *47*, (12), 6358-6367.
14. Kim, S.-K.; Kannan, K., Perfluorinated Acids in Air, Rain, Snow, Surface Runoff, and Lakes: Relative Importance of Pathways to Contamination of Urban Lakes. *Environ. Sci. Technol.* **2007**, *41*, (24), 8328-8334.

15. So, M. K.; Taniyasu, S.; Yamashita, N.; Giesy, J. P.; Zheng, J.; Fang, Z.; Im, S. H.; Lam, P. K. S., Perfluorinated Compounds in Coastal Waters of Hong Kong, South China, and Korea. *Environ. Sci. Technol.* **2004**, *38*, (15), 4056-4063.
16. Yamashita, N.; Kannan, K.; Taniyasu, S.; Horii, Y.; Petrick, G.; Gamo, T., A global survey of perfluorinated acids in oceans. *Marine Pollution Bulletin* **2005**, *51*, (8), 658-668.
17. Langer, V.; Dreyer, A.; Ebinghaus, R., Polyfluorinated Compounds in Residential and Nonresidential Indoor Air. *Environ. Sci. Technol.* **2010**, *44*, (21), 8075-8081.
18. Haug, L. S.; Huber, S.; Becher, G.; Thomsen, C., Characterisation of human exposure pathways to perfluorinated compounds - Comparing exposure estimates with biomarkers of exposure. *Environ. Int.* **2011**, *37*, (4), 687-693.
19. Jogsten, I. E.; Nadal, M.; van Bavel, B.; Lindstrom, G.; Domingo, J. L., Per- and polyfluorinated compounds (PFCs) in house dust and indoor air in Catalonia, Spain: Implications for human exposure. *Environ. Int.* **2012**, *39*, (1), 172-180.
20. Hurley, M. D.; Sulbaek Andersen, M. P.; Wallington, T. J.; Ellis, D. A.; Martin, J. W.; Mabury, S. A., Atmospheric Chemistry of Perfluorinated Carboxylic Acids: Reaction with OH Radicals and Atmospheric Lifetimes. *J. Phys. Chem. A* **2004**, *108*, (4), 615-620.
21. Stemmler, I.; Lammel, G., Pathways of PFOA to the Arctic: variabilities and contributions of oceanic currents and atmospheric transport and chemistry sources. *Atmos. Chem. Phys.* **2010**, *10*, (20), 9965-9980.
22. Hori, H.; Hayakawa, E.; Einaga, H.; Kutsuna, S.; Koike, K.; Ibusuki, T.; Kiatagawa, H.; Arakawa, R., Decomposition of Environmentally Persistent Perfluorooctanoic Acid in Water by Photochemical Approaches. *Environ. Sci. Technol.* **2004**, *38*, (22), 6118-6124.
23. Foreman, E. S.; Kapnas, K. M.; Murray, C., Reactions between Criegee Intermediates and the Inorganic Acids HCl and HNO<sub>3</sub>: Kinetics and Atmospheric Implications. *Angew. Chem. Int. Ed.* **2016**, *55*, (35), 10419-10422.
24. Criegee, R., Mechanism of Ozonolysis. *Angew. Chem. Internat. Edit.* **1975**, *14*, (11), 745-752.
25. Criegee, R.; Wenner, G., Die Ozonisierung des 9,10-Oktalins *Liebigs. Ann. Chem.* **1949**, *564*, (1), 9-15.
26. Osborn, D. L.; Taatjes, C. A., The physical chemistry of Criegee intermediates in the gas phase. *Int. Rev. Phys. Chem.* **2015**, *34*, (3), 309-360.
27. Khan, M. A. H.; Percival, C. J.; Caravan, R. L.; Taatjes, C. A.; Shallcross, D. E., Criegee intermediates and their impacts on the troposphere. *Environmental Science: Processes & Impacts* **2018**, *20*, (3), 437-453.
28. Lin, J. J.-M.; Chao, W., Structure-dependent reactivity of Criegee intermediates studied with spectroscopic methods. *Chem. Soc. Rev.* **2017**, *46*, (24), 7483-7497.
29. Taatjes, C. A., Criegee Intermediates: What Direct Production and Detection Can Teach Us About Reactions of Carbonyl Oxides. *Annu. Rev. Phys. Chem.* **2017**, *68*, (1), 183-207.
30. Taatjes, C. A.; Shallcross, D. E.; Percival, C. J., Research frontiers in the chemistry of Criegee intermediates and tropospheric ozonolysis. *Phys. Chem. Chem. Phys.* **2014**, *16*, (5), 1704-1718.
31. Shallcross, D. E.; Taatjes, C. A.; Percival, C. J., Criegee intermediates in the indoor environment: new insights. *Indoor Air* **2014**, *24*, (5), 495-502.
32. Percival, C.; Welz, O.; Eskola, A. J.; Savee, J. D.; Osborn, D. L.; Topping, D. O.; Lowe, D.; Utembe, S.; Bacak, A.; McFiggans, G.; Cooke, M.; Archibald, A. T.; Jenkin, M.; Derwent, R. G.; Riipinen, I.; Mok, D.; Lee, E. P. F.; Dyke, J.; Taatjes, C. A.; Shallcross, D. E., Regional and Global Impacts of Criegee Intermediates on Atmospheric Sulphuric Acid Concentrations and First Steps of Aerosol Formation. *Faraday Discuss.* **2013**, *165*, 45-73

33. Archibald, A. T.; Cooke, M. C.; Utembe, S. R.; Shallcross, D. E.; Derwent, R. G.; Jenkin, M. E., Impacts of mechanistic changes on HO<sub>x</sub> formation and recycling in the oxidation of isoprene. *Atmos. Chem. Phys.* **2010**, *10*, 8097-8118.
34. Utembe, S. R.; Cooke, M. C.; Archibald, A. T.; Jenkin, M. E.; Derwent, R. G.; Shallcross, D. E., Using a reduced Common Representative Intermediates (CRIv2-R5) mechanism to simulate tropospheric ozone in a 3-D Lagrangian chemistry transport model. *Atmos. Environ.* **2010**, *44*, (13), 1609-1622.
35. Utembe, S. R.; Cooke, M. C.; Archibald, A. T.; Shallcross, D. E.; Derwent, R. G.; Jenkin, M. E., Simulating secondary organic aerosol in a 3-D Lagrangian chemistry transport model using the reduced Common Representative Intermediates mechanism (CRI v2-R5). *Atmos. Environ.* **2011**, *45*, (8), 1604-1614.
36. Welz, O.; Savee, J. D.; Osborn, D. L.; Vasu, S. S.; Percival, C. J.; Shallcross, D. E.; Taatjes, C. A., Direct Kinetic Measurements of Criegee Intermediate (CH<sub>2</sub>OO) Formed by Reaction of CH<sub>2</sub>I with O<sub>2</sub>. *Science* **2012**, *335*, 204-207.
37. Taatjes, C. A.; Welz, O.; Eskola, A. J.; Savee, J. D.; Scheer, A. M.; Shallcross, D. E.; Rotavera, B.; Lee, E. P. F.; Dyke, J. M.; Mok, D. K. W.; Osborn, D. L.; Percival, C. J., Direct Measurements of Conformer-Dependent Reactivity of the Criegee Intermediate CH<sub>3</sub>CHOO. *Science* **2013**, *340*, (6129), 171-180.
38. Barton, C. A.; Botelho, M. A.; Kaiser, M. A., Solid Vapor Pressure and Enthalpy of Sublimation for Perfluorooctanoic Acid. *J. Chem. Eng. Data* **2008**, *53*, 939-941.
39. Kaiser, M. A.; Larsen, B. S.; Kao, C.-P. C.; Buck, R. C., Vapor Pressures of Perfluorooctanoic, -nonanoic, -decanoic, -undecanoic, and -dodecanoic Acids. *J. Chem. Eng. Data* **2005**, *50*, 1841-1843.
40. Khan, M. A. H.; Gillespie, S. M. P.; Razis, B.; Xiao, P.; Davies-Coleman, M. T.; Percival, C. J.; Derwent, R. G.; Dyke, J. M.; Ghosh, M. V.; Lee, E. P. F.; Shallcross, D. E., A modelling study of the atmospheric chemistry of DMS using the global model, STOCHEM-CRI. *Atmos. Environ.* **2016**, *127*, 69-79.
41. Khan, M. A. H.; Jenkin, M. E.; Foulds, A.; Derwent, R. G.; Percival, C. J.; Shallcross, D. E., A modeling study of secondary organic aerosol formation from sesquiterpenes using the STOCHEM global chemistry and transport model. *J. Geophys. Res. Atmos.* **2017**, *122*, (8), 4426-4439.
42. McGillen, M. R.; Curchod, B. F. E.; Chhantyal-Pun, R.; Beames, J. M.; Watson, N.; Khan, M. A. H.; McMahon, L.; Shallcross, D. E.; Orr-Ewing, A. J., Criegee Intermediate-Alcohol Reactions, A Potential Source of Functionalized Hydroperoxides in the Atmosphere. *ACS Earth Space Chem.* **2017**, *1*, (10), 664-672.
43. Vereecken, L., The reaction of Criegee intermediates with acids and enols. *Phys. Chem. Chem. Phys.* **2017**, *19*, (42), 28630-28640.
44. Chen, L.; Huang, Y.; Xue, Y.; Cao, J.; Wang, W., Effect of oligomerization reactions of Criegee intermediate with organic acid/peroxy radical on secondary organic aerosol formation from isoprene ozonolysis. *Atmos. Environ.* **2018**, *187*, 218-229.
45. Moshhammer, K.; Jasper, A. W.; Popolan-Vaida, D. M.; Wang, Z. D.; Shankar, V. S. B.; Ruwe, L.; Taatjes, C. A.; Dagaut, P.; Hansen, N., Quantification of the Keto-Hydroperoxide (HOOCH<sub>2</sub>OCHO) and Other Elusive Intermediates during Low-Temperature Oxidation of Dimethyl Ether. *J. Phys. Chem. A* **2016**, *120*, (40), 7890-7901.
46. Anglada, J. M.; Crehuet, R.; Francisco, J. S., The Stability of  $\alpha$  - Hydroperoxyalkyl Radicals. *Chemistry - A European Journal* **2016**, *22*, (50), 18092-18100.
47. Vereecken, L.; Nguyen, T. L.; Hermans, I.; Peeters, J., Computational study of the stability of  $\alpha$ -hydroperoxyl- or  $\alpha$ -alkylperoxyl substituted alkyl radicals. *Chem. Phys. Lett.* **2004**, *393*, (4), 432-436.
48. Meloni, G.; Zou, P.; Klippenstein, S. J.; Ahmed, M.; Leone, S. R.; Taatjes, C. A.; Osborn, D. L., Energy-resolved photoionization of alkyl peroxy radicals and the stability of their cations. *J. Am. Chem. Soc.* **2006**, *128*, (41), 13559-13567.

49. Watson, J. G.; Chow, J. C.; Park, K.; Lowenthal, D. H.; Park, K., Nanoparticle and ultrafine particle events at the Fresno Supersite. *Journal of the Air & Waste Management Association* **2006**, *56*, (4), 417-430.
50. Topping, D.; Barley, M.; Bane, M. K.; Higham, N.; Aumont, B.; Dingle, N.; McFiggans, G., UManSysProp v1.0: an online and open-source facility for molecular property prediction and atmospheric aerosol calculations. *Geosci. Model Dev.* **2016**, *9*, (2), 899-914.
51. Barley, M. H.; McFiggans, G., The critical assessment of vapour pressure estimation methods for use in modelling the formation of atmospheric organic aerosol. *Atmos. Chem. Phys.* **2010**, *10*, (2), 749-767.
52. O'Meara, S.; Booth, A. M.; Barley, M. H.; Topping, D.; McFiggans, G., An assessment of vapour pressure estimation methods. *Phys. Chem. Chem. Phys.* **2014**, *16*, (36), 19453-19469.
53. Wallington, T. J.; Schneider, W. F.; Worsnop, D. R.; Nielsen, O. J.; Sehested, J.; Debruyne, W. J.; Shorter, J. A., The Environmental Impact of CFC Replacements - HFCs and HCFCs. *Environ. Sci. Technol.* **1994**, *28*, (7), A320-A326.
54. Zhao, R.; Kenseth, C. M.; Huang, Y.; Dalleska, N. F.; Kuang, X. M.; Chen, J.; Paulson, S. E.; Seinfeld, J. H., Rapid Aqueous-Phase Hydrolysis of Ester Hydroperoxides Arising from Criegee Intermediates and Organic Acids. *J. Phys. Chem. A* **2018**, *122*, (23), 5190-5201.
55. Atkinson, R.; Baulch, D. L.; Cox, R. A.; Crowley, J. N.; Hampson, R. F.; Hynes, R. G.; Jenkin, M. E.; Rossi, M. J.; Troe, J., Evaluated kinetic and photochemical data for atmospheric chemistry: Volume II – gas phase reactions of organic species. *Atmos. Chem. Phys.* **2006**, *6*, 3625-4055.
56. US EPA *Estimation Programs Interface Suite™ for Microsoft® Windows v. 4.11*, United States Environmental Protection Agency: Washington, DC, USA, 2012.
57. Østerstrøm, F. F.; Wallington, T. J.; Sulbaek Andersen, M. P.; Nielsen, O. J., Atmospheric Chemistry of (CF<sub>3</sub>)<sub>2</sub>CHOCH<sub>3</sub>, (CF<sub>3</sub>)<sub>2</sub>CHOCHO, and CF<sub>3</sub>C(O)OCH<sub>3</sub>. *J. Phys. Chem. A* **2015**, *119*, (42), 10540-10552.